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(21) International Application Number: PCT/US97/18279 (22) International Filing Date: 10 October 1997 (10.10.97) (30) Priority Data: 08/729,264 10 October 1996 (10.10.96) US (71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (72) Inventors: CLEMMER, Paul, Gene; 128 Royal Parkway, W. Williamsville, NY 14221 (US). LOGSDON, Peter, Brian; 38 East Royal Hill Drive, Orchard Park, NY 14127 (US). PHAM, Hang, Thanh; Apartment 1, 96 Sundridge Drive, Amherst, NY 14228 (US). (74) Agent: CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (C.A. McNally), P.O. Box 2245, 101 Columbia Road, Morristown, NJ 07962-2245 (US).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, GH, HU, ID, IL, IS, JP, KP, KR, LK, LR, LS, LT, LV, MG, MK, MN, MW, MX, NZ, PL, RO, RU, SD, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS FOR SEPARATING PENTAFLUOROETHANE AND CHLOROPENTAFLUOROETHANE (57) Abstract The present invention pertains to a process for separating pentafluoroethane from a mixture with chloropentafluoroethane. A mixture of pentafluoroethane and chloropentafluoroethane is contacted with an entraining agent to form an azeotrope of the entraining agent and chloropentafluoroethane. Subsequently the pentafluoroethane is separated from the binary azeotrope of chloropentafluoroethane and entraining agent by distillation. Distillation is conducted such that the azeotrope of chloropentafluoroethane and entraining agent is removed as an overhead distillation fraction and the pentafluoroethane is removed as a bottoms distillation fraction.		

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PROCESS FOR SEPARATING PENTAFLUOROETHANE AND CHLOROPENTAFLUOROETHANE

Field of the Invention

The present invention pertains to a process for separating pentafluoroethane
5 ("HFC-125") from chloropentafluoroethane ("CFC-115"). More particularly, the
invention relates to a process for separating pentafluoroethane from
chloropentafluoroethane by distillation.

Background of the Invention

HFC-125 is a non-chlorine containing fluorocarbon that is especially useful as a
10 refrigerant, blowing agent, propellant, fire extinguishing agent and sterilant carrier gas.
HFC-125 may be prepared by hydrofluorinating tetrachloroethylene by various known
processes which result in a mixture containing HFC-125, CFC-115 and other fluorinated
compounds.

Unfortunately, the mixture of HFC-125 and CFC-115 forms an azeotrope at
15 atmospheric pressure and a near-azeotrope at elevated pressures. The boiling points of
these halogenated hydrocarbons are close, -48.5°C for HFC-125 and -38.7°C for
CFC-115, and their relative volatility is below 1.1 at concentrations of HFC-125 greater
than 87.5 mole percent, and below 1.01 at concentrations above 95 mole percent. These
boiling points and relative volatilities indicate that it is extremely difficult to recover
20 substantially pure HFC-125 from such mixtures by simple distillation and azeotropic
distillation.

A key problem when considering an azeotropic distillation process is discovering
an entraining agent, which agent undergoes a non-ideal interaction with a component, that
will sufficiently aid the desired separation process. The present invention employs an
25 entraining agent that forms an azeotrope with CFC-115, which azeotrope boils at a
temperature lower than HFC-125. It has been found that CFC-115 can efficiently and
effectively be removed from HFC-125 by azeotropic distillation with such an entraining
agent.

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Summary of the Invention

The invention provides a process for separating HFC-125 from a mixture of HFC-125 and CFC-115 which comprises contacting a mixture comprising HFC-125 and CFC-115 with an effective amount of an entraining agent to form an azeotrope of
5 CFC-115 and the entraining agent which azeotrope has a boiling point of about -48.5°C or less at atmospheric pressure.

The invention also provides a process for separating HFC-125 from an azeotropic mixture of HFC-125 and CFC-115 which comprises contacting a mixture comprising HFC-125 and CFC-115 with an effective amount of HFC-32 to form an azeotropic
10 mixture of CFC-115 and HFC-32.

The invention further provides a process for the purification of HFC-125 by removing CFC-115 therefrom which comprises adding to the impure HFC-125 a component which undergoes a non-ideal interaction with CFC-115 and/or with the azeotrope of CFC-115 and HFC-125 such that the volatility of CFC-115 and/or the
15 azeotrope of CFC-115 and HFC-125 relative to bulk HFC-125 is increased and distilling the mixture.

Detailed Description of Invention and the Preferred Embodiments

It has been discovered that HFC-125 may be efficiently purified, or separated, from a mixture of HFC-125 and CFC-115 by the use of an entraining agent that forms an
20 azeotrope with CFC-115. In the process of the invention, an entraining agent that forms an azeotrope with CFC-115 is added to a mixture of HFC-125 and CFC-115. Typically, the mixture of HFC-125 and CFC-115 will be the result of the hydrofluorination of tetrachloroethylene. However, the process of the invention is useful for any mixture of HFC-125 and CFC-115, especially azeotropic mixtures of HFC-125 and CFC-115. The
25 process is most effectively used for HFC-125/CFC-115 mixtures in which the weight of HFC-125 is about 90 weight percent or more.

Entraining agents useful in the invention are any agents that form azeotropes, preferably minimum boiling azeotropes so that the entraining agent/CFC-115 azeotrope

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can be separated from HFC-125. By minimum boiling is meant an azeotrope that boils at a temperature less than the boiling point of its individual components. Useful entraining agents for this invention non-exclusively include difluoromethane ("HFC-32"),

1,1,1-trifluoroethane ("HFC-143a") and mixtures thereof. The azeotropes

- 5 HFC-32/CFC-115 and HFC-143a/CFC-115 are known azeotropes with boiling points less than the boiling point of HFC-125/CFC-115, which is approximately -48.7° C at 1 atm. pressure, and HFC-125. A mixture of entraining agents may also be used, as long as the entraining agent mixture with CFC-115 has a boiling point below that of HFC-125. Illustrative mixtures suitable for use as entraining agents include, without limitation,
- 10 HFC-125/HFC-32 and HFC-125/HFC-143a.

- An effective amount of entraining agent is used which amount is an amount effective to form a minimum boiling azeotrope with CFC-115. The precise amount of agent used will depend on the entraining agent used. The weight ratio of the entraining agent to the amount of CFC-115 to be removed is typically in the range of from about 2:1
- 15 to about 500:1. Higher ratios may be used to minimize the amount of CFC-115 left in HFC-125, especially when the resulting entraining agent/HFC-125 mixture is a desired product, as is the case for HFC-32/HFC-125 and HFC-143a/HFC-125, which are commercial refrigerant azeotropic blends. Where the entraining agent is HFC-32, the preferred weight ratio is at least about 0.5:1. For HFC- 143a, the preferred ratio is at least
- 20 about 1.3:1. The methods of this invention can treat any mixture of HFC-125 and CFC-115, provided the above weight ratios of entraining agent to CFC-115 are used.

- The entraining agent is added so that the separation of HFC-125 from CFC-115 is optimized. Optimization occurs when the maximum efficiency in separation, or the minimum amount of CFC-115 in the bottoms, is achieved while energy and capital costs
- 25 along with entraining agent loss are minimized.

Any convenient means for separating the HFC-125 from the CFC-115/entraining agent azeotrope may be used. Preferably the HFC-125 is then separated from the azeotrope of CFC-115 and entraining agent by distillation. The separating may be conducted in a standard distillation column in which the azeotrope of CFC-115 and

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entraining agent is removed as an overhead distillation fraction and the HFC-125 is removed as a bottoms distillation fraction. Because not all of the HFC-125 may be separated from the CFC-115 by addition of the entraining agent, some HFC-125 may exit the column with the CFC-115/entraining agent azeotrope. The entraining agent/CFC-115 azeotrope can be optionally treated to recover and reuse the entraining agent. Also, if the entraining agent/CFC-115 stream contains HFC-125, the entraining agent/CFC-115 overhead stream may be treated by any convenient method to recover the HFC-125. Additionally, the entraining agent may form a mixture with the HFC-125 and exit with the HFC-125. For example, if HFC-32 or HFC-143a are used as the entraining agents, the HFC-125 distillation fraction may be a mixture of HFC-32/HFC-125 or HFC-32/HFC-143a.

Generally, the distillation is conducted at a temperature below the boiling point of HFC-125 at the distillation pressure. Preferably, the distillation is conducted at a temperature that is about 0.2 to about 50° Below the boiling point of HFC-125 at the distillation pressure, which may be subatmospheric to 500 psia.

It may be preferable in practice to employ more than a single distillation column or treatment to effect the separation of HFC-125 from CFC-115. Before adding the entraining agent, the HFC-125/CFC-115 mixture may be treated to concentrate the CFC-115 content, for example, by pressure swing distillation as described in U.S. Patent 5,346,595, which is incorporated in its entirety herein by reference. The entraining agent can also be used on a HFC-125/CFC-115 mixture following a separate treatment which reduces the CFC-115 content before treatment with the entraining agent. In any of these embodiments, the resulting entraining agent/CFC-115 mixture can be treated by physical or chemical means to recover the entraining agent and/or convert the CFC-115 to a useful product such as conversion to a hydrofluorocarbon by hydrogenation or reaction with a reducing agent.

The following non-limiting examples served to illustrate the invention.

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Example 1

A batch still equipped with a packed column of approximately 40 stages was charged with a mixture of 98.2 wt.% HFC-125, 0.7 wt.% CFC-115, 1 wt.% HFC-32 and approximately 0.1 wt.% of higher-boiling halogenated hydrocarbon impurities. The still
5 was operated at total reflux for a time sufficient to obtain stable conditions with reboiler temperature of 2°C. Still pressure was 89 psig. Samples of the column top vapor and reboiler liquid were removed and analyzed by gas chromatography and found to have the following compositions:

Column top vapor: 49.5 wt.% HFC-125; 9 wt.% CFC-115; 41.5 wt.% HFC-32

10 Reboiler liquid: 98.7 wt. % HFC-125; 0.5 wt. % CFC-115; 0.5 wt. % HFC-32.

The still was then warmed to a reboiler temperature of 20°C and allowed to reach stable conditions. Still pressure was 175 psig. Samples of the column top vapor and reboiler liquid were removed and analyzed by gas chromatography and found to have the following compositions:

15 Column top vapor: 50.1 wt. % HFC-125; 9.4 wt.% CFC-115; 40.5 wt.% HFC-32.

Reboiler liquid: 98.4 wt.% HFC-125; 0.6 wt. % CFC-115; 0.6 wt.% HFC-32

Example 2

A mixture containing 64 wt % HFC-32, 26 wt. % CFC-115, and 10 wt. % HFC-125 was loaded into a still equipped with a packed column of approximately 140
20 stages. The still was run at atmospheric pressure and at total reflux for the first 1.5 hours and at about 20:1 reflux ratio later while withdrawing vapor from the condenser. A first sample of the overhead vapor was withdrawn and collected, with a weight equal to 0.35 wt. % of the initial charge. A second sample of the overhead vapor was withdrawn and collected, with a weight equal to 0.53 wt. % of the initial charge. A third sample of the
25 overhead vapor was then withdrawn and collected. Analyses of the three samples by gas chromatography gave the following results:

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First sample: 41.1 wt. % HFC-32; 0.7 wt. % HFC-125; 58.2 wt. % CFC-115

Second sample: 39.4 wt. HFC-32; 60.6 wt % CFC-115

Third sample: 39.4 wt % HFC-32; 60.6 wt. % CFC-115

The second and third sample analyses demonstrate that there is no ternary azeo-
5 trope between 32/115/125. The mixture fractionates and the lower boiling 32/115 distills
out at the top of the column.

Example 3

A mixture containing 48.7 wt. % HFC-143a, 49.1 wt. % HFC-125, and 2.2 wt.%
CFC-115 was charged to the still described in Example 2. The still was operated at atmos-
10 pheric pressure and total reflux for 1.5 hours, then a first sample was withdrawn from the
still overhead vapor at a reflux ratio of about 20:1 until 11% of the initial charge had been
withdrawn. A second sample was obtained at similar conditions until an additional 15% of
the initial charge had been withdrawn. The still was then shut down and a sample of the
residual liquid in the still was obtained. Analyses of the three samples by gas chroma-
15 tography gave the following results:

First sample: 25 wt.% HFC-125; 50 wt. % HFC-143a; 25 wt. % CFC-115.

Second sample: 42 wt.% HFC-125; 57 wt. % HFC-143a; 1 wt. % CFC-115.

Residual liquid. 54 wt. % HFC-125; 46 wt. % HFC-143a.

This example demonstrates that CFC-115 can be completely removed from a
20 mixture of 125/143a/115 by distillation.

Example 4

A mixture containing 0.7 wt. % CFC-115 and 99.3 wt. % HFC- 125 was fed to a
first continuous distillation column with about 50 stages operating at about 25 psia. An
overhead stream containing 5 wt. % CFC-115 and 95 wt. % HFC-125 was removed and
25 fed continuously to a second continuous distillation column with 50 stages operating at

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about 160 psia. The overhead stream from the second distillation column was recycled to the first Column. A sample of the bottoms stream of this second distillation column containing 9 wt. % CFC-115 and 91 wt. % HFC-125 was obtained and fed to a third continuous distillation column along with a stream of HFC-32. The weight ratio of HFC-32 to the 125/115 stream was 1:5 and the weight ratio of HFC-32: HFC-115 was 2.2:1. Analysis by GC of the overhead and bottoms streams of the third distillation column gave the following analyses:

Overhead: 33 wt. % HFC-125, 21 wt. % CFC-115; 46 wt. % HFC-32

Bottoms: 93 wt. % HFC-125; 0.07 wt. % CFC-115; 7 wt. % HFC-32. This demonstrates that HFC-32 can be used as an entraining agent to remove CFC-115 from a CFC-115/HFC-125 mixture in a continuous distillation column.

Example 5

A mixture containing 8 wt. % CFC-115 and 92 wt. % HFC-125 was fed to the same third distillation column described in Example 5 along with a stream of HFC-143a. The weight ratio of HFC-143a to the 125/115 stream was 1.3:1 and the weight ratio of HFC-143A:HFC-115 was 16:1. Analysis by GC of the overhead and bottoms streams of the third distillation column gave the following analyses:

Overhead: 50.6 wt. % HFC-125; 14.0 wt. % CFC-115; 35.4 wt. % HFC-143a

Bottoms: 54.9 wt. % HFC-125; 4.7 wt. % CFC-115; 40.4 wt. % HFC-143a

This demonstrates that HFC-143a can be used as an entraining agent to remove CFC-115 from a CFC-115/HFC-125 mixture in a continuous distillation column.

What is claimed is:

1. A process for the purification of pentafluoroethane by removing chloro-
pentafluoroethane therefrom which comprises adding to the impure pentafluoro-
ethane a component which undergoes a non-ideal interaction with chloro-
5 pentafluoroethane and/or with the azeotrope of chloropentafluoroethane and
pentafluoroethane such that the volatility of chloropentafluoroethane and/or the
azeotrope of chloropentafluoroethane and pentafluoroethane relative to bulk
pentafluoroethane is increased and distilling the mixture.
2. The process of claim 1 in which the component is difluoromethane.
- 10 3. The process of claim 1 in which the component is 1,1,1-trifluoroethane.
4. A process for separating pentafluoroethane from a mixture of pentafluoroethane
and chloropentafluoroethane which comprises contacting a mixture comprising
pentafluoroethane and chloropentafluoroethane with an entraining agent to form a
binary azeotrope of chloropentafluoroethane and the entraining agent which
15 azeotrope has a boiling point of about -48.5°C or less at atmospheric pressure.
5. The process of claim 4 further comprising subsequently separating pentafluoro-
ethane from the binary azeotrope of chloropentafluoroethane and entraining agent.
6. The process of claim 4 wherein the entraining agent comprises a component
selected from the group consisting of difluoromethane, 1,1,1-trifluoroethane and
20 mixtures thereof.
7. The process of claim 5 wherein the separating is conducted by distillation.
8. A process for separating pentafluoroethane from an azeotropic mixture of
pentafluoroethane and chloropentafluoroethane which comprises contacting a
mixture comprising pentafluoroethane and chloropentafluoroethane with an
25 effective amount of difluoromethane to form an azeotropic mixture of
chloropentafluoroethane and difluoromethane.

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9. The process of claim 8 comprising subsequently separating pentafluoroethane from the binary azeotrope of chloropentafluoroethane and difluoromethane by distillation.
10. The process of claim 5 further comprising subsequently separating chloro-
5 pentafluoroethane from the entraining agent.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/386 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 03936 A (DU PONT) 6 February 1997 see claim 1	4-7
X	WO 95 27689 A (ICI PLC) 19 October 1995 see claims	1, 2
A	WO 96 06063 A (ICI PLC) 29 February 1996 see page 2, line 23 - line 29; claim 1	1, 3
A	US 5 087 329 A (FELIX VINCI M) 11 February 1992 see the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/US 97/18279

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